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FLUOR

March 30, 2005

Fernald Closure Project
Letter No. C:PROJ:2005-0023

Mr. John Sattler
U. S. Department of Energy
Ohio Field Office - Fernald Closure Project
175 Tri-County Parkway
Cincinnati, Ohio 45246

Dear Mr. Sattler:

**CONTRACT DE-AC24-01OH20115, FLUOR FERNALD SILOS 1 AND 2 TREATMENT
PROCESS – LEAD LEACHABILITY**

The Department of Energy (DOE) recently requested information on the Silos 1 and 2 chemical stabilization process as it relates to the leachability of heavy metals in the final waste form. This correspondence provides a response to the DOE request.

Background

As you are aware, the Silos 1 and 2 residues have been designated as 11e(2) byproduct materials by DOE and Congress. As byproduct wastes, the K-65 materials are excluded from the definition of solid waste and therefore exempt from consideration as a hazardous waste under the Resource Conservation and Recovery Act (RCRA). The Explanation of Significant Differences (ESD) for Operable Unit 4 Silos 1 and 2 Remedial Action⁽¹⁾ documents this classification and establishes the regulatory requirements for the implementation of the final remedy to address the silo residues. The ESD, which was approved by DOE and the United States Environmental Protection Agency (USEPA) in November 2003 after formal state and public review, established that "it is now permissible to permanently dispose of the treated Silos 1 and 2 residues at the Nevada Test Site (NTS) without applying the Toxicity Characteristic Leaching Procedure (TCLP) limits as quantitative performance standards, and that a commercial facility may also be able to accept the Silos 1 and 2 materials in the near future. Based on this new information, DOE and USEPA conclude that the TCLP-based waste treatment performance standard, adopted in both the 1994 Record of Decision (ROD) and the 2000 Operable Unit 4 Silos 1 and 2 ROD Amendment as a facility-specific relevant and appropriate requirement for treatment, is no longer necessary to maintain compliance with disposal facility waste acceptance requirements, either at NTS or an appropriately permitted commercial disposal facility. DOE and the USEPA are therefore removing the quantitative TCLP performance standard as a relevant and appropriate regulatory requirement for execution of the Silos 1 and 2 selected remedy."

As the basis for this change, the ESD stated that, "regardless of the modification to quantitative performance standards or off-site disposal options, the Silos 1 and 2 material will continue to be treated by chemical stabilization with no changes to the physical characteristics of the final waste form, the associated transportation risks, or the disposal method. Reducing the leachability of metals will continue to be a goal of the treatment process with the primary focus still being the reduction of the direct radiation levels and moisture content of the material to facilitate safe and efficient transportation and disposal. The treatability study data collected from past and future studies will be used both to optimize the chemical stabilization process requirements and to obtain the maximum reasonably obtainable reduction in leachability."

Lead is one of the major components comprising as much as 13 percent by weight of the Silos 1 and 2 material as indicated by Remedial Investigation/Feasibility Study (RI/FS) data. The leachability of lead ranged from 137 to 445 mg/l (ppm) in tests conducted by the University of Cincinnati (UC)⁽²⁾ on Fluor Fernald, Inc. (Fluor Fernald) Silos 1 and 2 untreated material. The toxicity limit for lead in a solid waste regulated under RCRA is 5.0 mg/l as measured through use of the TCLP test.

General Approach to the Maximum Reasonably Obtainable Reduction in Leachability

Consistent with the ESD, the Silos 1 and 2 chemical stabilization process has been designed to achieve the maximum reasonably obtainable reduction in the leachability of lead. The design of the chemical stabilization process was based upon treatability study data, which utilized the TCLP test as the relative measure of the reduction in the leachability of lead in the treated waste form. To obtain the required reduction in the leachability of lead, Fluor Fernald has designed and will utilize a series of process controls to yield a final waste form that minimizes lead leachability.

The formulation for treatment of the Fluor Fernald Silos 1 and 2 material that was used as a basis for the current design and process control procedures was developed to achieve a treated product that is self-leveling, exhibits no free water after curing, and minimizes leaching of lead. The *Silos 1 and 2 Stabilization Treatability Study Final Report* 40700-RP-0010⁽²⁾ [the University of Cincinnati study] provides the results of these studies. The purpose of the treatability study was to establish a grout formulation, including the proportions of cement and flyash, to serve as the design basis of the full scale Silos 1 and 2 treatment process. The tests were performed using actual materials obtained from Silos 1 and 2.

The solubility of lead compounds has been extensively studied and the effect of pH on the leachability of lead is well known. The solubility of materials is controlled by a physical constant known as the Solubility Product that describes the amount of material that will dissolve in water at specified conditions. A number of authors⁽³⁾, including publications by the USEPA⁽⁴⁾ report that the solubility of many common metal hydroxides exhibit a "valley" as a function of pH. Figure 1⁽⁵⁾ illustrates the effect of pH on lead solubility. The solubility of lead decreases with increasing pH, and is minimal between pH 8 and pH 12 in aqueous systems. The solubility (leachability) of lead from stabilized lead-bearing wastes is reviewed in *Chemical Fixation and Solidification of Hazardous Wastes* by Jesse R. Conner⁽⁵⁾. Combined data from leachability testing on numerous stabilized lead-bearing materials show

that in the range of pH 8-12, the maximum concentration of dissolved lead in the leachate is approximately 2 parts per billion (ppb), three orders of magnitude lower than the 5.0 mg/l regulatory limit for lead TCLP.

The Fernald Silos 1 and 2 Treatability Study

The UC Treatability Study demonstrated that the Fluor Fernald Silos 1 & 2 material exhibits the same type of behavior as the numerous published test results on lead solubility. The Silos 1 and 2 material shows a "valley" as the pH rises and minimum solubility of lead from the waste occurs in the pH range 8-to-11.5, Figure 2⁽¹⁾ shows the behavior of the Fluor Fernald K-65 material to be similar to the published data (Figure 1). The Treatability Study determined that adding cement at a value of 8 - 12 % of the final batch weight of the treated material, or grout, will result in a pH in the range of 8-to-11.5 in the final TCLP leachate, and will minimize lead leaching. The treatability study contains all of the required support data on the reduction of lead leachability for the recipe for the Silos 1 and 2 stabilization process.

The USEPA SW-846 TCLP Test Method 1311⁽⁶⁾ describes steps to select the pH of the extraction solution for the leachate tests, based on the alkalinity of the waste to be tested. The nature of the Silos 1 and 2 grout product requires the leaching test to be done in "Extraction Fluid #2" that has a pH of 2.88. The Silos 1 and 2 grout formula is designed to adjust the final pH of the TCLP extraction fluid to a condition that minimizes the leachability of lead. The selected 8-12 weight % cement in the Silos 1 and 2 grout formula is the amount required to neutralize the acid in Extraction Fluid #2 and to increase the basicity of the TCLP filtrate to the pH range of 8-12 known to minimize lead leaching. Figure 2 confirms that the stabilization recipe for treatment of the Silos 1 and 2 material complies with the intent of "maximum reasonably obtainable reduction in leachability" required by the ESD.

The Bottom Line on Lead Leachability from Treated Material

The published treatability study on actual Fluor Fernald Silos 1 and 2 material shows that, regardless of waste loading, the application of 8-12 weight % cement in the treatment process consistently produces a treated waste form that achieves maximum reduction of lead leachability. It is a fact of chemistry that when Silos 1 and 2 material is treated with 8-12 weight % cement, the result is a pH in the range of 8-11.5 for the TCLP leachate from the final waste form and minimum leachability of lead. When this proportion of cement is maintained, the TCLP leachability of lead is minimized, and any increases in overall batch waste loading will not increase the leachability of lead. Thus, one key element of the Silos 1 and 2 process operating philosophy⁽⁷⁾ is to apply the necessary controls in the process to yield a treated waste product that contains a consistent weight percent of cement in the range of 8 to 12%.

Silos 1 and 2 Process Implementation and Control

The Silos 1 and 2 treatment process has been designed to fulfill the ESD objective to achieve the "maximum reasonably obtainable reduction in leachability" by implementing process controls to provide a reasonable assurance that the cement content in the final formulation for a given batch will be between 8 and 12 weight percent. These process

controls include the following:

- In-line instruments have been installed to provide critical data on the radium and solids content of the individual feed tanks prior to batch formulation. The microwave densitometers, which have been calibrated against the surrogate material, have proven to provide reliable estimates of the solids content of a given feed tank. Reliable estimates of the feed tank solids content are critical to ensuring the elimination of freestanding liquids and to the production of a final batch mix with a given weight percent of cement. The microwave densitometers have been shown to yield real-time estimates of the solids content of a feed tank within 1 to 3 percent (absolute) of the empirically measured value. These densitometers will be re-calibrated against the K-65 residues upon introduction of this material into the system. The operation of the microwave densitometers is guided by Silos Procedure⁽⁹⁾ 11-C-374 *Silos 1 and 2 Product Grout Preparation Normal Operating Procedure, Rev 6*.
- Prior to the treatment of a batch of silo material, Procedure 11-C-374 requires the operator to be in possession of a Product Batch Recipe approved by the Shift Supervisor, and to verify that the slurry system is operating and ready to support operations. Figure 3 shows an example of an approved Product Batch Recipe.
- To prepare for treatment operations, the Procedure requires the operator to enter information into the computer-controlled batch recipe-builder Programmable Logic Controllers (PLC) system to specify the volume and density of the product required and the density of the slurry to be treated. The Procedure further requires the operator to enter data to prescribe the individual steps to be followed for preparing a batch consisting of the slurry plus cement and flyash. The operator enters recipe setpoints into the HMI (Human-Machine Interface), as well as the tolerances specified in the Product Batch Recipe, including:
 - A. Container volume
 - B. Density of final mixture
 - C. Container % full
 - D. Specific gravity of solids in slurry
 - E. The sequence and number of steps for addition or mixing of the recipe
 - F. The tolerance limits for each recipe ingredient or step.

The operator typically sets the tolerance on the quantity of cement at ± 30 lb. The individual recipe steps set by the operator typically consist of the following steps:

1. Add Slurry
2. Start Mixer
3. Add Fly Ash
4. Mix Step #1
5. Add Cement
6. Final Mixing

In some cases the steps for cement addition and fly ash addition may be

interchanged in sequence at the discretion of the Shift Supervisor.

- The Silos 1 and 2 Product Mixer System is equipped with a computer-controlled recipe-building PLC system programmed with an algorithm that automatically determines the recipe for treatment of the batch to meet treatment requirements. The PLC applies formulas based on the treatability study and on confirmatory data from other independent laboratory testing. Fluor Fernald has conducted validation and verification⁽⁷⁾ of the PLC processor system and assured that it accurately applies the design recipe formula. The PLC uses the algorithm and the input data and automatically calculates the quantities of each component for the recipe, including the quantity of slurry and each ingredient for the batch, and displays the details on the HMI as a Product Mixer Recipe Formulation report. The PLC automatically sets the cement ingredient at 10% of the total batch weight. In addition to recipe information on the individual components for the treatment batch, the HMI also displays the projected properties of the batch, including radium concentration, total batch weight, waste loading and treated waste solids. Figure 4 in the Appendix provides an example of a Product Mixer Recipe Formulation of the type displayed to operators. The information describes the properties of the expected treatment batch, and is used by operators to confirm that proceeding with mixing the batch will produce a product that meets design requirements.
- Prior to initiating the operation to mix a batch of treated material, Procedure 11-C-374 requires the operator to verify that the following parameters are within the waste acceptance limits:
 - A. Radium concentration in the feed slurry is less than 100,000 pCi/g
 - B. Total Batch weight is less than 17,000 lbs
 - C. Waste Loading is greater than or equal to 14% and less than or equal to 32%
 - D. Treated Waste Solids Wt% is greater than or equal to 54% and less than or equal to 69%

The operator also checks to assure that the batch recipe formulation will provide the target value of 10% cement in the treated batch.

- Once the operator verifies that conditions are acceptable per procedure to proceed with treatment of the slurry, the operator initiates the treatment evolution for the batch by instructing the PCL to conduct the first step: transfer of the recipe-computed quantity of slurry from the feed tank to the mixer, typically an amount in the range of 7,500 to 10,000 lb for feed slurries with 36-43 weight % solids (the target operating range). The in-line totalizer instrument in the feed line measures the volume of slurry added to the mixer, and an in-line densitometer in the feed system measures the % solids of the slurry. The computer-controlled system uses the % solids and volume information to compute and control the total weight of slurry added to the mixer. In addition to this in-line source of information, load cell instruments on the mixer provide an independent measurement of the weight of slurry added to the mixer (as well as providing the weights of other ingredients added in the subsequent steps in the recipe).

- When the first step of slurry addition to the mixer is complete, the system computes the weight and the operator can ascertain the quantity of slurry added to the mixer.
- The automated Product Mixer System initiates Step 2 to start operation of the mixer, and then initiates Step 3 of a typical batch preparation to add fly ash (or cement) to the operating mixer. The treatment system automatically operates screw feeders in the fly ash weigh hoppers located above the mixer to dispense the fly ash into the mixer, and to automatically monitor, record, meter and limit the quantity added using information from load cells on the fly ash hopper. Typically, the tolerance on the quantity of fly ash set by the operator is 75 lb. For a typical batch, this tolerance in the fly ash ingredient amounts to approximately ± 0.4 % of the final weight of the treated batch.
- Step 4 of the batch preparation consists of a period for mixing of the first ingredient into the slurry, during which time information is displayed on the HMI monitors for use by the operator in verifying addition of the correct amount of fly ash to satisfy the recipe.
- The automated Product Mixer System then initiates Step 5 of a typical batch preparation by manually instructing the system to add cement (or fly ash) to the operating mixer containing the slurry and fly ash. The treatment system automatically operates screw feeders in the cement weigh hoppers located above the mixer to dispense the cement ingredient into the mixer, and to automatically monitor, control and record the quantity added using information from load cells on the hopper. The quantity of cement - the key parameter required for control of lead leachability - that is added by the automated Product Mixer System is 10 weight % of the final batch weight⁽⁷⁾. For a typical batch, the tolerance in the cement ingredient amounts to approximately ± 0.2 % of the final weight of the treated batch. In addition to information from instruments on the hopper, load cell instruments on the mixer provide an independent measurement of the weight of the cement ingredient used in the preparation of the batch.
- The load cells that provide information for control of the ingredients in the Recipe Formulation of the batch are calibrated instruments and are checked weekly⁽⁹⁾.
- The final Step 5 is mixing to complete the batch. A typical batch weighs approximately 16,500 lb.
- When the treatment batch is complete, the PLC automated system produces a Mixer Batch Data Report which provides detail information on the treatment recipe consisting of the actual batch weight data based on load cell instruments on the mixer, as well as the independent information from load cells on the individual fly ash and cement ingredient hoppers, the weight of slurry treated, the weight of the fly ash ingredient measured in the mixer, weight of the cement ingredient measured in the mixer, the actual weight % cement in the batch, the actual % waste loading, the actual weight of K-65 material treated, and the actual volume of treated material produced from the batch. Figure 5 shows an example of a Mixer Batch Report.

Copies of these batch reports will be maintained as part of the supporting file for each container produced from the Silos 1 and 2-treatment process.

In order to assure reliable scale-up of the treatment recipe from the treatability study to actual operations-scale recipe formulation, Fluor Fernald plans to sample treated material from the first five containers produced by the Product Mixer System. These samples will be analyzed to assure that the Product Mixer System operates to design, and that treatment of the Silos 1 and 2 material complies with all requirements, including demonstration of a meaningful reduction in the leachability of lead. Fluor Fernald plans no other regular sampling and analysis for leachability during routine treatment operations.

Summary

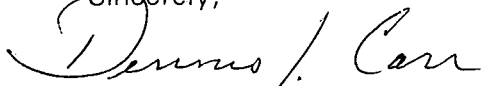
Fluor Fernald has established rigorous, independently reviewed plans and procedures for implementing operations for the treatment of the Silos 1 and 2 material to the requirements established by the ESD. Fluor Fernald project documentation including operating philosophies and procedures clearly specify material batch conditions and the treatment recipe⁽⁸⁾.

In summary, treatability studies performed on actual Silos 1 and 2 untreated waste demonstrate that the materials exhibit significant leachability of lead as measured through the TCLP test methods. These studies also indicate that the silo materials can be expected to behave consistent with previous literature based studies, which examined the reduction of lead leachability in waste materials. These studies indicate that the key parameter in reducing the leachability of lead in a given waste form is the control of the pH of the TCLP extract. This control is accomplished through the addition of pre-measured weight percentages of Portland cement. Regardless of the waste loading, as long as the overall weight percent of Portland cement is maintained between 8 and 12%, the leachability of lead in the final waste form will be minimized. Treatability studies performed on silo materials confirm that maintaining an 8 to 12 weight percent of cement in the grout formulation will minimize the leachability of lead in the final waste form regardless of the waste loading. In order to fulfill the ESD requirement for the production of a waste form which yields the maximum reasonably achievable reduction in lead leachability, Fluor Fernald has invoked a series of process controls aimed at ensuring that a given batch will contain between 8 and 12 weight percent of Portland cement. Samples will be collected from the first five containers produced in the Silos 1 and 2 process for TCLP analysis to provide confirmation that the scale up of the system continues to yield the desired reduction in lead leachability. No batch-specific sampling will be conducted for lead leachability over and above the first five containers.

Experience gained in January, February and March 2005 from operational demonstrations with surrogate material at various waste loadings and batch sizes has confirmed that the process controls in place will operate as expected to produce treated material to recipe specifications. Fluor Fernald has confidence that this process control-based approach will provide the necessary assurances that the ESD obligations for minimizing lead leachability have been successfully achieved.

If you require additional information or clarification, please contact Dennis Carr at (513) 648-3799.

Sincerely,



Dennis J. Carr
Sr. Project Director
Silos Project

DJC:ced
Attachment(s)

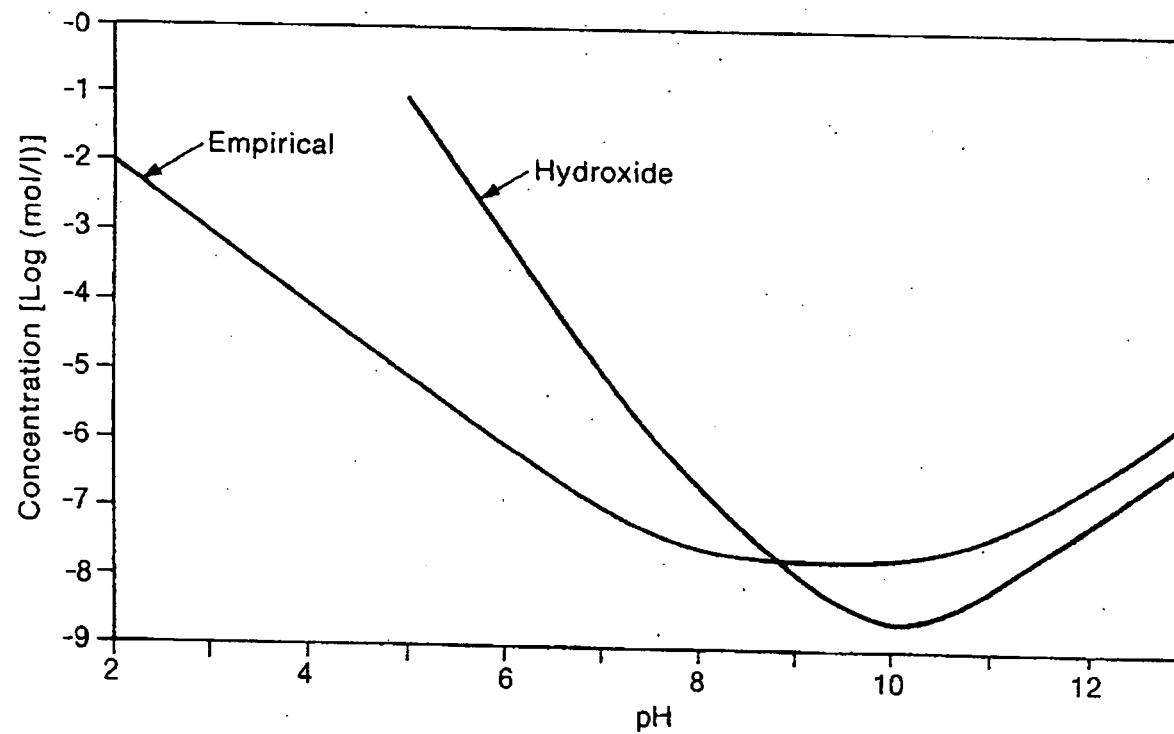
c: Steve Beckman, MS20
Joe Desormeau, DOE-OH/FCP
Ralph E. Holland, DOE Contracting Officer, DOE-OH/FCP
Jamie Jameson, MS01
Shelby Kawa, DOE-OH
Don Luken, MS24
Con Murphy, MS77
John North, MS20
Paul Pettit, MS24
Johnny Reising, DOE-OH/FCP
Dennis Sizemore, Fluor Fernald, Inc. Prime Contract, MS 1
DOE Records Center
Letter Log Copy, MS 1
Project Number 40000/1.1
Administrative Record, MS 78

APPENDIX

REFERENCES

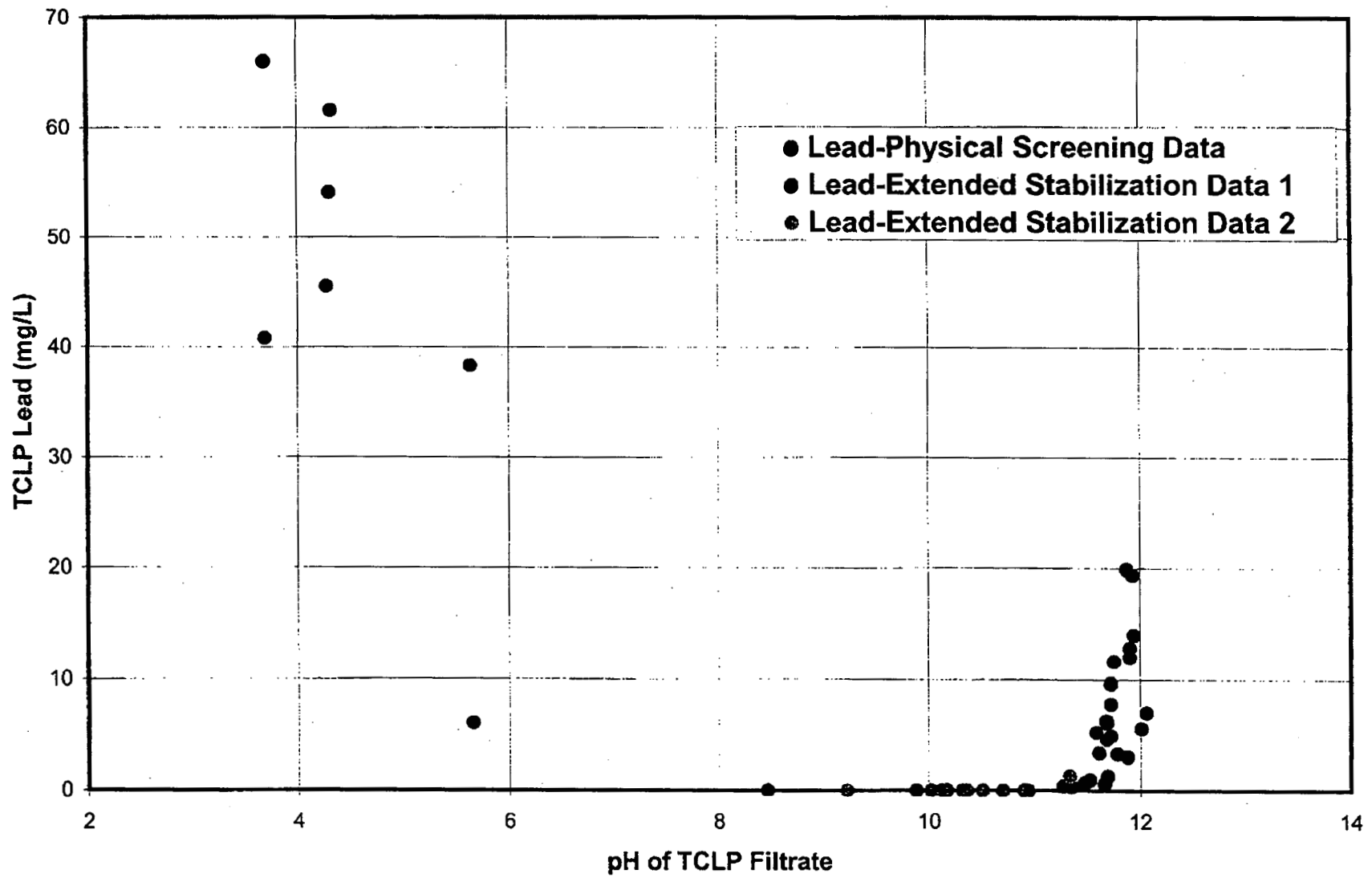
- 1) *Final Explanation of Significant Differences for Operable Unit 4 Silos 1 and 2 Remedial Actions*, 40750-RP-0038, October 2003
- 2) *Silos 1 & 2 Stabilization Treatability Study Final Report* 40700-RP-0010, Rev. 0, Ayen, R.J., and Reiser, L, University of Cincinnati September 2002
- 3) Cote, P. *Contaminant Leaching from Cement-Based Waste Forms Under Acidic Conditions*, Ph.D. Thesis, McMaster University, Hamilton, Ont., Canada 1986
- 4) U.S. EPA, Federal Register. **52**(155): 29999 (Aug. 12, 1987)
- 5) Conner, Jesse R., *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990
- 6) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, EPA Publication SW-846 Revision 5, Method 1311: Toxicity Characteristic Leaching Procedure, April 1998
- 7) Silos 1 and 2 Project Control System Philosophy, 40750-RP-0054, Section 6 Processor System (System 17), pp 72-214,
- 8) *Silos 1 and 2 Waste Treatment and Packaging User's Manual for Grout Recipe Building and Troubleshooting*, 40750-MAN-0244, Rev. 0 Jan. 2005
- 9) Procedure 11-C-374 *Silos 1 and 2 Product Grout Preparation Normal Operating Procedure*, Rev 6, March 11, 2005

Figure 1 (from Conner⁽⁵⁾)



Solubility of lead vs. pH in a cement/flyash CFS system.

Figure 2. TCLP Lead vs pH of TCLP Filtrate[from (2)]



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Figure 3 **Example of** **Approved Product** **Batch Recipe**

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03/05-06/05 NIGHT SHIFT

ATTACHMENT 4 - PRODUCT BATCH RECIPE

Container Volume:	187.6	Specific Gravity of Solids:	2.0	Product Fill Line (Circle one)	A <u>B</u> or C
Density of Final Mixture:				Feed Slurry Density lbs/ft ³	
Container Percent Full:	92			Type of Recipe (Circle one)	<u>Original</u> / Revised
Air entrainment in Mix:				Batch Number (if known)	

Mix formulation										Weight per batch, lbs								
K-65 Feed Solids Wt%	K-65 Pounds Per Gallon	Radium Conc in slurry pCi/g	Treated Waste Solids Wt%	Flush H2O per batch gallons	Formulation Density Lbs/ft ³	Flush H2O Gallons	Feed Slurry Lbs	Feed Slurry Gallons	FlyAsh Lbs	Cement Lbs	Waste Loading	Radium conc in Recipe pCi/g	Total Batch Weight lbs	Feed Slurry Lbs	Feed Slurry Gallons	Flush H2O Gallons	FlyAsh Lbs	Cement Lbs
		95,000																

Steps	Step Name	Setpoints					Limits		
		Percent	Gallons	Pounds	Minutes	RPM	Tolerance	Minimum	Maximum
1	ADD SLURRY STEP #1	100					10 gal		
2	MIXER START STEP					15			
3	FLY ASH STEP #1	100					75 lb		
4	MIX STEP #1				0.5				
5	CEMENT STEP #1	100					30 lb 30 lb		
6	FINAL MIX STEP				5				

Analytical Lab Representative

Paul J. Pettit
 PAUL PETTIT

Date 03/05/05

Shift Supervisor

Doug Miller

Date: 3-5-05

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Figure 5 Example Mixer Batch Report

****TOD Means Time of Day hh:mm.**
****Date Means mm/dd/yy delete leading 0.**

Batch screen

Product Sum wt	16373
Variance %	-2

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